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TO: G. W. Irving, Jr., Assistant Chief of Bureau, AIC, Washington, D. C.
FROM: J. S. Ard, Analytical Chemist, Biologically Active Compounds Div., ARC, Beltsville, Maryland
SUBJECT: Report of a Symposium on Molecular Structure and Spectroscopy, held at Ohio State University, Columbus, Ohio, June 13-18, 1949.

Summary: Most attention is given to reporting on applications and instrumentation, though a large proportion of the program was devoted to very involved mathematical interpretations of data on simple molecules. New radiation instruments coming into commercial development were discussed by representatives of the manufacturers with exhibits and working models; the Perkin-Elmer split-beam infrared (IR) spectrophotometer was of particular interest. Micro-wave, Raman, ultra-violet, gas analyzers, and reference data systems were also discussed. A considerable number of the more important personalities in the IR field attended, and there were opportunities to hear them in informal discussions.

Raman Spectra: Raman data often supplements IR well; some information analagous to that of the IR regions as far as 50 microns can be obtained with glass prisms and cells, also aqueous solutions can be used. Isotopes are detected only under the most favorable conditions. Fluorescene is a difficulty and even such contaminations as from a cork are disturbing (apparently only freshly distilled samples give the best results). Raman scans have fewer lines than IR because the combination and overtone complexities are less. Since the peaks are sharper and better separated, there is less need in quantitative analysis for consideration of the partial densities of each component of mixtures. Water-cooled electrode pools of the Hg-arc now allow a steadier and brighter source. $NaNO_2$ solution filters, and polaroids before and after the sample, cross oriented, relatively diminish Hg-line disturbances.

The installations are expensive, especially the new fast ones with photomultiplier detection and recording, costing about $24,000. One difficulty is that the detector needs cooling in liquid nitrogen (2 l./8 hr. day) to reduce the noise level satisfactorily. The Lane-Wells recording instrument takes about 15 ml. samples (1-4.5 ml. in special arrangements), and scans the 200-1500 $cm.^{-1}$ region in 6-1/2 to 35 minutes. The source is photocell-monitored for constancy.

Microwave Studies: As a microwave cource, magnetrons are used. The fundamental wave is far too long and is rejected by filters, leaving only a minor proportion of the harmonic energy (10^{-11} at 7th harmonic) to pass as the useful power at the ultra-high frequencies. The cells described were about 15 foot tubes with a Stark-effect high potential

vane down the center. Crystal detectors were usually used, though heat detectors were necessary at the higher frequency limits. The energy of measured absorptions changes rapidly with wavelength, that at 1-2 mm. being 1000 times that at 1-2 cm., and it is understood that the absorption coefficients are very weak and not measured with much quantitative accuracy. They are located as to position with extreme accuracy (frequencies to 7 places), and fine structure is highly resolved. No commercial microwave spectrometers are available, but approximately 15 locations in the United States have special installations. An authoritative source of information to us in this field would be the Bureau of Standards, and possibly the Naval Research Laboratory.

Isotopes (C^{13} & ^{14}, O^{18}, S^{33} & ^{34}, I^{129} B^{10}, and Se^{77}) have been studied; $OC^{12}S$, for example gives a band at 24,179.62 megacycles, and $OC^{13}S$ at 24,176.07. Microwave spectra is characteristic of the whole rather than fraction parts of the molecule, and an isotopic tracer substance may be lost if its parent molecule goes through transformations; this would be of advantage in the special case of determining if the labeled molecules act or are transported as the initial molecular identity. The molecule detected must have considerable unsymmetrical moment; CO_2 was specifically mentioned as having insufficient moment, and it is not practical to measure total isotopic carbon converted to this state.

All of the examples mentioned were simple molecules, about the complexity of methanol. The substance must be in the gaseous state in a very long cell, but micro quantities at low vapor pressures ("a few 0.01 mm.") are sufficient. It is understood that the size of the molecule is a limitation, even if sufficiently volatile. With methanol as an example, complex spectra without regional gaps was shown to exist from 37 to 320 microns.

Microwave data is of easier mathematical interpretation than that from electron diffraction. Interatomic distances of simple molecules can be determined to 0.01 Angstrom, dipole moments to about 1%, also conclusions can be drawn about the angle and character of bonds and various coupling and rotation-hindering effects.

IR Comparison Data and Plotting Systems: There is a pressing need for a universal system of recording IR data. The chief obstacle to a co-operative printing of the reference data pools is lack of agreement on whether the linear base scale should be in reciprocal centimeters or microns. The micron system won by vote here, but the question could not be considered as settled. In general, those with the highest standing and the most data to offer were emphatically in favor of the reciprocal centimeters, which is of easier physical interpretation and makes the identification of fundamental, combination, and overtone structures easier. On the other hand, it jams the significant bands together, spreads structureless portions across much of the graph, and does not harmonize well with the dispersion of prism materials and the need for less curvature in standardization graphs. Twin-beam instrument manufacturers supply cams for either system. Apparently considerable effort will be made to do as the vote directed and set up a system with a micron base. A card is planned with a punched border, a curve on one side, and data as source and properties on the other. A separate card is planned for literature

references. Due to the laborous work of regraphing and punching, the cost will be high it it needs to be supported by the few subscribers interested enough. It is hoped that some organication like the National Research Council will finance it. It seems unlikely that the frequency basis group will change to a micron system, and the project may have a difficult time without the support of both groups.

Instruments: National Technical Laboratories exhibited a new IR instrument to be produced. It runs the blank spectrum with the energy going into a selsyn generator and then to a wire recorder ("memory device"). Then on running the sample, it corrects for the recorded blank spectra. Some extra electrical noise accumulates, and it appears from the imposing electronic equipment that carrying out this rather simple idea had unexpected difficulties. Maintenance might be troublesome. Where the spectrometer part has been purchased, this extra equipment may be advisable, but it did not appear to be along the normal trend of developments. The price is expected to be around $10,000 including the spectrometer. Their IR3 large research instrument costs about $25,000 and is understood to have a 2-prism monochromator and to be too complex for prism changes.

Baird's instrument was described. They emphasize convenience, a good service plan, the ability to be used by untrained personnel, and the capacity for an enormous volume of work. It is understood that the slit is fixed and that the instrument is not very adaptable to special research problems such as where special wavelength regions need expanding with higher resolution. The optics are interchangeable (salt, KBr, LiF, KRS). They say the ease of scanning from 2-16 microns in 12 minutes brings a new and valuable attitude to the laboratory in which the IR is not just left to special needs but is used to replace a great volume of other work. Solvents and distillation fractions, even though they number 60 or more, may be individually checked. Price about $13,500.

There was some discussion of large special installations. Some are adaptable for both grating and prisms or have them in tandem. Usually these are of high dispersion and may have mechanical interchange of optics as by an elevator or ferris-wheel arrangement. Completion requires several years, and they evidently have troubles that have been better solved in standard models. The cost is excessive ("about $25,000 for the optical part, and this much more for the electrical accessories" - Hampton, U. S. Rubber Co.).

The Perkin-Elmer split-beam instrument, now orderable at about $11,000, was exhibited. It appears to be along the lines of normal development and to be a good, practical, well-engineered instrument with an extreme of scientific adaptability as well as the advantages of writing a finished linear-adjusted (cams) and blank-compensated spectra. The wavelength and slit widths read directly by two Veeder counters. A wide range of speed and resolution adjustments are selectable. One source and one detector are used, simplifying adjustment and maintenance. The beam is divided for sample and blank, and the blank beam is reduced to balance the sample beam by a system of horizontal multiple converging slits, which move across a vertical slit. The beams are combined alternatingly by a rotating mirror and are detected. The detector, by servo, moves the balancing mechanism to keep the AC component destroyed. A speed suppressor slows the whole mechanism at increments so that relatively more time is given to tracing the slopes

with fidelity. The first amplifier is located at the detector site to minimize the amplification of noise. Probably a great improvement is that the instrument is heated and thermostated at all times to 105° F., which protects the optics from humidity and keeps junction potentials constant; and then the motors and filaments help to heat the instrument instead of contributing to distortion. Perhaps the only criticisms are that it has three KBr lens and loses some of the advantages of an all-mirror system, that it may have some of the difficulties characteristic of the first model of a new series, and that no wave-length marker was observed (presumably there is one).

IR gas recorders have reached a stage of development whereby CO_2 can be recorded continuously to 1 PPM from 0-100. They have been found suitable for recording minute quantities from plant respiration. For the detector, the IR expanded gas actuates a diaphram which is the condenser plate of a microphone. Mica windows can be used.

The Golay IR detecting system was exhibited. It is made by the Eppley Laboratories, Inc., in sizes to replace thermocouples in the various spectrometers. It performs at extreme cycle ranges (to 1000/sec. with practical efficiency, limit about 5000/sec.), and at extreme wavelengths (10-39 microns). The detector, in a daylighted room, detects the change of IR when a hand is put in front of it, not by interception but by the IR from the hand. Inside it has a small light, which is directed at a photocell by way of a reflecting flexible diaphram and bracketing multiple slit gratings. The gratings just prevent light passing when the diaphram is undisturbed, but when IR activates the gas in a small cell, this disturbs the diaphram and upsets the balance of the light bars on the grating. It appears to convert IR to visible light, and the light is registered on a photocell. Dr. Golay also exhibited a system for increasing the energy through the prism by a multiple slit combination, and a replacement for make-and-break contacts with light choppers and photocells. These mechanisms are novel and effective when correctly adjusted; and are regarded by some as the long-sought way past the present IR detector limitations, and by others as peculiar and impractical inovations. Certainly they will have important special uses.

Sources of Information: Some men are listed who spoke and seemed especially qualified and practical, their accessibility being considered in the selection. If IR manuscripts contain controversial matter, it would seem desirable to duscuss it with one of the following before publication.

At National Bureau of Standards, Wash. 25, D. C., Drs. Curtis J. Humphreys and E. K. Plyler. These men are of top quality with generalized knowledge and long experience in IR, including theory, interpretation, instrumentation, and applications, for all regions. Dr. E. Carrol Creitz is very good on optical, electrical, and plotting problems in connection with the Perkin-Elmer instrument, and on high pressure cells and the spectra of petroleum gases.

At Naval Research Lab., Wash. 20, D. C., Don C. Smith. Good at analytical interpretations.

At Perkin-Elmer Corp., Grenbrook, Conn., John U. White. Exceptional technical knowledge in the whole field.

At Baird Associates, Cambridge, Mass., W. Lewis Hyde. Technical knowledge of Barid instrument, a shrewd observer of what is practical in the field.

At U. S. Rubber Co., Passaic, N. J., Robert R. Hampden. Practical knowledge from applications in the rubber field.

At American Cyanamid, Calco, and Dow are groups which seemed more exceptional as teams than as individuals. Cyanamid probably has the largest collection of IR reference data in the world.

Henry H. Grimm, NRL, Washington 20, D. C., is accessible for microwave questions, but qualifications are unknown.

Wallace R. Brode, author of book on general spectroscopy, is at Bureau of Standards.

Miscellaneous Information: IR is becoming more important in the inorganic field; many of these substances give spectra when powdered and mulled; inorganic buffer salts are frequent contaminants of IR spectra of biological samples.

The structure of glasses can be examined by reflection spectra, and a preliminary etching tends to remove those units not definitely a part of the network. Polytrifluorochloroethylene, of the Kellog Co., is a Teflon-like plastic recently released; it is suitable for transmissions out to 4-5 microns (IR cells, Raman tubes, etc.); its milkyness is removed by heating and quenching. IR polarizers are coming into frequent use, and their decrease of certain bands often given useful information. Confirming older explanations, "Cold" rubber has been shown to be more trans, "hot" more random, and balata and such more cis; rubber crystalizes most rapidly about -25° C.

In regard to education, textbooks, and the availability of trained personnel in IR, the situation appears unsatisfactory. Those away from the few centers where instruments have accumulated have numerous difficulties and few places to go for practical answers. Schools appear to be weak in teaching IR applications and more inclined to substitute a preponderance of black-board mathematics.

The rotation-vibration spectra of the simple gases (H_2) can be obtained in very long cells (75 ft., multiple reflections, 10 atmospheres). IR can be piped through long copper guides by multiple reflections at low incidence. Twin-beam instruments appear to be frequently set to register slightly less than zero where the solvent deadens the ability to record true, identifying these portions.

In regard to the Perkin-Elmer 12C instrument, it was learned that the auto-stop switch is a left-over from DC and can as well be taped up; that no danger to the thermocouple results on leaving it connected and trying the strongest test signal (100 microvolts); that thermocouples need re-evacuation at the factory about every 6-12 months at about $50 cost (our experience indicates that they can go longer); that accessories such as an adjustable cell and adaptations for microquantities are coming out; and that a larger Solar plus ballast lamp has been found desirable for globar power.

12-Washington Office
1-Eastern Laboratory
1-Northern Laboratory
1-Southern Laboratory
1-Western Laboratory
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